

~~ajouter le mélange des monomères correspondant au troisième stade (C) et les (co)polymériser pour obtenir celui-ci,~~

chaque étape de polymérisation étant effectuée en émulsion, dans un milieu aqueux, en présence d'un initiateur de radicaux libres et d'un agent émulsifiant, le produit obtenu à l'issue de ces trois étapes se présentant sous la forme de latex.

9. Composition thermoplastique consistant en un mélange comprenant, pour 100 parties en poids :

- de 10 à 99 parties en poids d'un polymère thermoplastique rigide d'au moins un monomère choisi parmi les méthacrylates d'alkyle, dont le groupe alkyle comprend de 1 à 4 atomes de carbone, et les hydrocarbures vinylaromatiques ou d'un polymère de plus de 50% en poids d'au moins l'un de ces monomères et d'au moins un autre monomère copolymérisable à insaturation monoéthylénique ; et
- de 90 à 1 parties en poids de l'interpolymère tel que défini à l'une des revendications 1 à 7.

10. Composition thermoplastique selon la revendication 9, caractérisée par le fait que la combinaison des stades (A) et (B) de l'interpolymère représente de 18 à 40% en poids de la composition thermoplastique totale.

11. Tout article façonné obtenu au moyen de la composition thermoplastique telle que définie à l'une des revendications 9 et 10.

#### Claims

1. Multilayer composite interpolymer characterised in that it comprises:

A - a first relatively soft elastomeric stage which has a glass transition temperature lower than or equal to 25°C, polymerised, in the absence of any crosslinking or grafting monomer, by starting with a mixture of monomers comprising, per 100 parts by weight:

(a) from 50 to 100 parts by weight of at least one alkyl or aralkyl acrylate; and,

(b) from 0 to 50 parts by weight of at least one other monomer containing ethylenic unsaturation copolymerisable with the said acrylate, chosen from alkyl methacrylates in which the alkyl group contains from 1 to 8 carbon atoms, alkoxy acrylates, cyanoethyl acrylate, acrylonitrile, acrylamide, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, acrylic acid, methacrylic acid, as well as vinylaromatic hydrocarbons such as styrene,  $\alpha$ -methylstyrene and vinyltoluene,

B - a second elastomeric stage which in itself has a glass transition temperature lower than or equal to 25°C, polymerised in the presence of the product of the first stage by starting with a mixture of monomers comprising, per 100 parts by weight:

(a) from 50 to 99.9 parts by weight of at least one main monomer chosen from conjugated dienes and alkyl or aralkyl acrylates;

(b) from 0 to 49.9 parts by weight of at least one monomer containing monoethylenic unsaturation copolymerisable with the said main monomer, chosen from alkyl methacrylates in which the alkyl group contains from 1 to 8 carbon atoms, alkoxy acrylates, cyanoethyl acrylate, acrylonitrile, acrylamide, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, acrylic acid, methacrylic acid, as well as vinylaromatic hydrocarbons such as styrene,  $\alpha$ -methylstyrene and vinyl toluene,

(c) from 0.05 to 8 parts by weight of at least one crosslinking monomer; and

(d) from 0.05 to 6 parts by weight of at least one grafting monomer; and,

C - a third, relatively hard, nonelastomeric stage which in itself has a glass transition temperature higher than 25°C, polymerised in the presence of the products of the first and the second stages by starting with a mixture of monomers comprising, per 100 parts by weight:

(a) from 85 to 99.9 parts by weight of at least one main monomer chosen from alkyl methacrylates in which the alkyl group contains from 1 to 4 carbon atoms, and vinylaromatic hydrocarbons,

(b) from 0.1 to 10 parts by weight of at least one copolymerisable monomer containing monoethylenic unsaturation copolymerisable with the said main monomer chosen from acrylic monomers such as alkyl acrylates in which the alkyl group contains from 1 to 8 carbon atoms, alkoxy acrylates, cyanoethyl acrylate, acrylonitrile, acrylamide, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, acrylic acid and methacrylic acid

(c) from 0 to 5 parts by weight of at least one chain limiter agent,

the stages (A), (B) and (C) representing, per 100 parts by weight of the said interpolymer, 3 to 80 parts

by weight, 10 to 60 parts by weight and 10 to 60 parts by weight respectively.

2. Interpolymer according to Claim 1, characterised in that when it is in the form of pulverulent particles, the diameter of these particles lies in the range from 40 to 500 nm.
3. Interpolymer according to either of Claims 1 and 2, characterised in that the crosslinking monomer (c) of stage (B) is chosen from polyol polymethacrylates and polyacrylates, polyvinylbenzenes and vinyl acrylate and methacrylate.
4. Interpolymer according to one of Claims 1 to 3, characterised in that the grafting monomer (d) of stage (B) is chosen from allyl, methallyl or crotyl esters of carboxylic acids or diacids containing  $\alpha,\beta$  unsaturation, allyl ether, methallyl ether and crotyl vinyl ether, allyl thioether, methallyl thioether and crotyl vinyl thioether; N-allyl-, methallyl- or crotylmaleimide, vinyl esters of 3-butenic acid and of 4-pentenoic acid, triallyl cyanurate, O-allyl, methallyl or crotyl O-alkyl, aryl, alkaryl or aralkyl P-vinyl, allyl or methallyl phosphonate, triallyl, trimethallyl or tricrotyl phosphate; O-vinyl, O,O-diallyl, dimethallyl or dicrotyl phosphate, cycloalkenyl esters of acrylic acid, of methacrylic acid, of maleic acid, of fumaric acid, of itaconic acid, bicyclo[2.2.1]hept-5-en-2-yl esters of acrylic acid, of methacrylic acid, of maleic acid, of fumaric acid and of itaconic acid, vinyl ethers and vinyl thioethers of cycloalkenols and of cycloalkene thiols and vinyl esters of cycloalkene carboxylic acids.
5. Interpolymer according to one of Claims 1 to 4, characterised in that the chain limiter agents (c) of stage (C) are chosen from mercaptans, polymercaptans, polyhalogenated compounds, diunsaturated monoterpenes and monounsaturated diterpenes.
6. Composite interpolymer according to one of Claims 1 to 5, characterised in that it is in the form of a latex with a concentration of 20 to 50 % by weight in water.
7. Composite interpolymer according to one of Claims 1 to 5, characterised in that it is in the form of a powder.
8. Process for the preparation of a multilayer interpolymer as defined in one of Claims 1 to 6, characterised in that it comprises the stages consisting in:
  - forming the polymer of the first stage (A) by (co)polymerisation of the monomers (a) and, if appropriate, (b),
  - adding the mixture of the monomers corresponding to the second stage (B) and (co)polymerising them to obtain the latter; and
  - adding the mixture of the monomers corresponding to the third stage (C) and (co)polymerising them to obtain the latter,each polymerisation stage being performed in emulsion, in an aqueous medium, in the presence of a free-radical initiator and of an emulsifying agent, the product obtained at the end of these three stages being in latex form.
9. Thermoplastic composition consisting of a mixture comprising, per 100 parts by weight:
  - from 10 to 99 parts by weight of a rigid thermoplastic polymer of at least one monomer chosen from alkyl methacrylates in which the alkyl group contains from 1 to 4 carbon atoms, and vinylaromatic hydrocarbons or of a polymer of more than 50 % by weight of at least one of these monomers and of at least one other copolymerisable monomer containing monoethylenic unsaturation; and
  - from 90 to 1 parts by weight of the interpolymer as defined in one of Claims 1 to 7.
10. Thermoplastic composition according to Claim 9, characterised in that the combination of the stages (A) and (B) of the interpolymer represents from 18 to 40 % by weight of the total thermoplastic composition.
11. Any shaped article obtained by means of the thermoplastic composition as defined in either of Claims 9 and 10.